

Method for cleaning film-forming apparatuses

This invention relates to a method for cleaning film-forming apparatuses. More specifically, this invention relates to a method for cleaning a film-forming apparatus after the apparatus has been used to form a film comprising ruthenium or solid ruthenium
5 oxide.

Ruthenium materials, such as ruthenium metal and solid ruthenium oxide such as ruthenium dioxide, are becoming increasingly important as component materials in semiconductor devices; they are used, for example, as electrode materials for semiconductor memories.

10 Films of ruthenium materials can be formed on semiconductor wafers by sputtering and chemical vapor deposition (CVD). During these film fabrication processes, ruthenium or ruthenium dioxide, as the case may be, is deposited not only on the semiconductor wafer target, but also on constituent members of the film-forming apparatus, for example, on the inner walls of the sputtering or CVD chamber
15 (collectively referred to below as the film-forming chamber) and on the semiconductor wafer mounting boat or susceptor, within conduits, and so forth. When these ruthenium-type deposits are not removed, they exfoliate from, for example, the inner walls of the film-forming chamber and in this manner are a cause of particle generation, thereby leading to a deterioration in the quality of the semiconductor thin films subsequently
20 formed on the semiconductor wafers. The film-forming apparatus must therefore undergo cleaning.

Patent Reference 1 describes the removal of ruthenium or solid ruthenium oxide (e.g., ruthenium dioxide) attached to the film-forming chamber by contact with aqueous

ceric ammonium nitrate solution. However, wet methods such as this are inconvenient in terms of handling and also provide a low removal efficiency.

In contrast to this, Patent Reference 2 describes a dry method that removes ruthenium metal as ruthenium tetroxide, a volatile compound. This is done by bringing
5 the ruthenium metal deposited on the inner walls of the film-forming chamber into contact with an atomic oxygen-donating gas, such as ozone.

Patent Reference 1

United States Patent Number 6,143,192

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Patent Reference 2

Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 10-30439 (30,439/1998)

15 The inventors carried out intensive research into the use of oxidizing gas (e.g., ozone) to remove ruthenium deposited on the inner walls of the film-forming chamber. As a result, it was discovered that, due to oxygen adsorbed to the film-forming chamber and oxygen from, for example, silicon oxide film formed on the semiconductor wafer, solid ruthenium oxide, such as ruthenium dioxide, is formed on the surface of ruthenium
20 metal that has become deposited on the inner walls of a film-forming chamber that has been used to form a ruthenium metal film. It was also found that this solid ruthenium oxide at the surface prevents removal of the ruthenium metal by ozone. This also

means that ozone is not highly effective for the removal of solid ruthenium oxide, such as ruthenium dioxide.

The object of this invention, therefore, is to provide an efficient method for cleaning film-forming apparatuses in order to remove a ruthenium-type deposit residing on a constituent member of a film-forming apparatus after said apparatus has been used to form a film comprising ruthenium or solid ruthenium oxide, wherein at least the surface region of the ruthenium-type deposit comprises solid ruthenium oxide.

The present inventors discovered that a particular film-forming apparatus can be very efficiently cleaned by

bringing the solid ruthenium oxide formed on the ruthenium metal into contact with a reducing gas that contains hydrogen or the hydrogen radical (reducing species), thereby reducing the solid ruthenium oxide to ruthenium metal, and subsequently bringing the ruthenium metal into contact with an oxidizing gas that contains an oxygenated compound (oxidizing species), e.g., ozone, and exhausting it from the system as a volatile ruthenium compound.

This reduction by reducing gas containing hydrogen or the hydrogen radical can of course also be applied to ruthenium-type deposits comprising solid ruthenium oxide. The ruthenium metal produced by this reduction can, as above, be brought into contact with oxidizing gas and removed from the system as a volatile ruthenium compound.

Thus, this invention provides a method for cleaning a film-forming apparatus in order to remove a ruthenium-type deposit residing on a constituent member of the film-forming apparatus after said apparatus has been used to form a film comprising ruthenium or solid ruthenium oxide, wherein at least the surface region of the

ruthenium-type deposit comprises solid ruthenium oxide, said method being characterized by

converting the aforesaid solid ruthenium oxide into ruthenium metal by bringing the ruthenium-type deposit into contact with a reducing gas that contains a
5 reducing species comprising hydrogen or the hydrogen radical,
subsequently converting the ruthenium metal into volatile ruthenium oxide by bringing the ruthenium metal into contact with an oxidizing gas that contains an oxidizing species comprising an oxygenated compound, and removing this volatile ruthenium oxide from the film-forming apparatus.

10 This invention can efficiently clean a film-forming apparatus in order to remove a ruthenium-type deposit residing on a constituent member of the film-forming apparatus after said apparatus has been used to form a film comprising ruthenium or solid ruthenium oxide, wherein at least the surface region of the ruthenium-type deposit comprises solid ruthenium oxide.

15 This invention is described more specifically hereinbelow.

This invention relates to a method for cleaning a film-forming apparatus in order to remove a ruthenium-type deposit residing on a constituent member of the film-forming apparatus after said apparatus has been used to form a film comprising ruthenium or solid ruthenium oxide, wherein at least the surface region of the ruthenium-type deposit
20 comprises solid ruthenium oxide.

The film-forming apparatus encompasses, for example, a film-forming chamber, the lines (conduits) that introduce and exhaust the CVD precursor gas and carrier gas, and so forth. In addition, there is disposed within the film-forming apparatus a mounting

member that carries or supports the semiconductor wafer that is the target of the intended film-formation process. This mounting member may be, for example, a boat in the case of a batch-type film-forming apparatus or a susceptor in the case of a single-wafer film-forming apparatus. The constituent members of the film-forming apparatus include the aforesaid film-forming chamber, conduits connected to the film-forming chamber, the semiconductor wafer mounting member, and so forth.

According to the present invention, the ruthenium-type deposit residing on a constituent member of the film-forming apparatus is first brought into contact with a reducing gas that contains hydrogen or the hydrogen radical (reducing species), thereby converting (reducing) the solid ruthenium oxide, e.g., ruthenium dioxide, to ruthenium metal. This reduction can be effected by passing the reducing gas within the film-forming apparatus.

This reducing gas can be composed of only hydrogen, but the hydrogen is preferably adequately diluted with an inert gas based on safety considerations. The reducing gas is preferably composed of inert gas that contains 1-5 volume% hydrogen. Nitrogen is particularly preferred for the inert gas.

The reduction is preferably carried out at 80°C-800°C and more preferably at 120°C-250°C. The pressure within the film-forming apparatus during reduction is preferably established at 0.01-1000 torr. The reduction can be completed in 0.5 to 50 minutes. This reduction converts the solid ruthenium oxide to ruthenium metal with the production of H₂O. Introduction of the reducing gas is halted when the reduction is finished.

The ruthenium metal afforded by the reduction is then brought into contact with oxidizing gas containing an oxygenated compound (oxidizing species). Prior to this, however, it is preferable based on safety considerations that the interior of the film-forming apparatus be purged post-reduction by the passage of an inert gas (preferably
5 nitrogen) in order to thoroughly discharge from the film-forming apparatus any residual hydrogen or hydrogen radical that may be present.

The oxidizing gas containing an oxygenated compound (oxidizing species) is passed through the film-forming apparatus after the hydrogen and hydrogen radical have been exhausted, i.e., substantially in the absence of hydrogen and hydrogen
10 radical. This passage of the oxidizing gas converts (oxidizes) the ruthenium metal into volatile ruthenium oxide (ruthenium tetroxide, etc.).

The oxygenated compound includes ozone (O_3), oxygen (O_2), nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), water vapor (H_2O), hydrogen peroxide (H_2O_2), and their mixtures wherein oxygen and ozone are preferred. The oxidizing gas
15 preferably contains at least 2 volume% ozone and preferably 2-5 volume% ozone. The oxidizing gas can be oxygen gas containing about 5% ozone as produced by a commercial ozone generator.

This oxidation can be run preferably at $0^{\circ}C$ - $150^{\circ}C$ and is more preferably run at room temperature ($20^{\circ}C$ - $30^{\circ}C$) without heating. This oxidation serves to convert the
20 ruthenium metal to volatile ruthenium oxide (ruthenium tetroxide).

The completion of this oxidation can be detected by monitoring production of the volatile ruthenium oxide. For example, the gas exhaust line from the film-forming

apparatus can be provided with a concentration detection unit that detects the concentration of the volatile ruthenium oxide in the exhaust gas stream from the film-forming apparatus. This concentration detection unit can comprise an ultraviolet spectrometer, Fourier-transform infrared spectrometer, Raman spectrometer, or other
5 known detection unit capable of measuring the concentration of the volatile ruthenium oxide. The point of oxidation completion is the point at which volatile ruthenium oxide is no longer detected by the concentration detection unit in the exhaust gas stream from the film-forming apparatus. The introduction of oxidizing gas can be stopped at this point. This concentration detection enables the start and completion of ruthenium metal
10 oxidation to be promptly comprehended. When during this cleaning by oxidation of the ruthenium metal cleaning does not advance due to the formation of a thin layer of oxide on the surface of the ruthenium metal, the introduction of the oxidizing gas can be halted, the interior of the film-forming apparatus can be thoroughly exhausted and purged with an inert gas such as nitrogen, and the above-described reduction and
15 oxidation can be repeated.

The volatile ruthenium oxide-containing exhaust gas stream from the film-forming apparatus is discharged from the system after, inter alia, the volatile ruthenium oxide has been removed by the usual means. However, it has been found that the volatile ruthenium oxide can be efficiently removed from the exhaust gas stream from the film-
20 forming apparatus by heating this exhaust gas from the film-forming apparatus (the first removal method) or by bringing the exhaust gas into contact with a decomposition catalyst comprising ruthenium metal or a solid ruthenium compound (the second removal method) that has been set up in advance.

The volatile ruthenium oxide is decomposed and removed in the first removal method by heating the exhaust gas stream from the film-forming apparatus. This thermal decomposition converts the volatile ruthenium oxide into solid ruthenium oxide, which undergoes deposition. Heating the exhaust gas stream from the film-forming apparatus to 50°C-800°C enables a much more effective decomposition and detoxification of the volatile ruthenium oxide. The exhaust gas stream from the film-forming apparatus is also preferably heated under a pressure of 0.01-1000 torr. The use of a heating temperature $\geq 100^{\circ}\text{C}$ also enables decomposition of ozone that may be present in the exhaust gas stream from the film-forming apparatus.

This thermal decomposition of the volatile ruthenium oxide can be carried out using a decomposition unit whose interior defines at least one flow path for the exhaust gas stream from the film-forming apparatus. A heater for thermal decomposition is elaborated over the circumference of this decomposition unit. This decomposition unit should have a structure that causes little pressure loss at the gas stream inlet and outlet, but the decomposition unit is not otherwise particularly specified. The decomposition unit can be constituted, for example, of a tubular body. This tubular body may define a single gas flow path in its interior or may define a plurality of gas flow paths in its interior, for example, as in a honeycomb structure. A decomposition unit whose interior defines a plurality of gas flow paths is preferred from the standpoint of decomposition efficiency. The decomposition unit can be made of heat-resistant material that is not corroded by the volatile ruthenium oxide (for example, quartz, stainless steel). The exhaust gas stream from the film-forming apparatus is introduced into the decomposition unit through an open end (gas inlet) thereof and flows within the

gas flow path(s) while being heated by the heater at the temperature cited above. The volatile ruthenium oxide decomposed within the decomposition unit is converted to solid ruthenium oxide that deposits on the inner walls of the decomposition unit. A gas stream from which the volatile ruthenium oxide has been removed is discharged from the other open end (outlet) of the decomposition unit. As discussed below, solid ruthenium oxide attached on the inner walls of the decomposition unit itself functions as a decomposition catalyst for the volatile ruthenium oxide. As a consequence, once solid ruthenium oxide produced by the heating-induced decomposition of the volatile ruthenium oxide has become deposited on the inner walls of the decomposition unit, the volatile ruthenium oxide can still be thoroughly decomposed even when the heating temperature is dropped.

In the second removal method, the exhaust gas stream from the film-forming apparatus is brought into contact with a particular decomposition catalyst that has been laid out in advance. The use of a decomposition catalyst enables a much more effective removal of the volatile ruthenium oxide than simple heating alone. Ruthenium metal or a solid ruthenium compound is used as this decomposition catalyst. The solid ruthenium compound can be exemplified by ruthenium dioxide and ruthenium trifluoride. Viewed from the perspective of the convenient recovery described below, this solid ruthenium compound is preferably the solid ruthenium oxide that is the decomposition product of the volatile ruthenium oxide.

When the exhaust gas stream from the film-forming apparatus is brought into contact with these decomposition catalysts, the volatile ruthenium oxide in the exhaust gas stream is converted to a solid ruthenium oxide that deposits on the decomposition

catalyst. This contact between the decomposition catalyst and exhaust gas stream from the film-forming apparatus can be carried out at pressures of 0.01-1000 torr.

The exhaust gas stream from the film-forming apparatus can be brought into contact with the decomposition catalyst at 0°C-800°C, but the volatile ruthenium oxide
5 can be thoroughly removed even at $\leq 300^\circ\text{C}$.

Contact between the exhaust gas stream from the film-forming apparatus and the decomposition catalyst is most preferably carried out by attaching the decomposition catalyst on the walls of the gas flow path(s) of a decomposition unit as described above in relation to the first removal method and then passing the exhaust gas stream through
10 said gas flow path(s).

The concentration of the volatile ruthenium oxide in the effluent gas stream from the decomposition unit can be monitored in order to set the initial conditions for decomposition of the volatile ruthenium oxide and in order to control the decomposition efficiency. This concentration monitoring can be conducted using the same unit for
15 detecting volatile ruthenium oxide as described above.

This invention is described in additional detail hereinbelow with reference to the drawings. The same reference symbols have been assigned to the same elements throughout all the drawings.

Figure 1 contains a block drawing that illustrates an example of a film-forming
20 apparatus that is provided with a system that successively implements cleaning of the film-forming apparatus and removal of volatile ruthenium oxide in accordance with the present invention.

The film-forming apparatus **10** is provided with a film-forming chamber **101**. Disposed within the film-forming chamber **101** is a wafer mounting platform **102** on which the semiconductor wafer (not shown) is mounted. A wafer heating unit (not shown) can be disposed within this wafer mounting platform **102**. A heating unit **103** is disposed on the circumference of the film-forming chamber **101** in order to heat the interior of the film-forming chamber **101** to a prescribed temperature. Components such as, for example, a conduit system, control valves, flow rate adjustment devices, and other necessary elements for introduction of the carrier gas and film-generating precursor gas are of course disposed at and around the film-forming apparatus **10**, but with the exception of the pump these are not shown for the sake of simplicity.

The system for cleaning the film-forming apparatus **10** includes a hydrogen cylinder **201** (reducing gas source) and an ozone generator **202** (oxidizing gas source). Hydrogen gas from the hydrogen cylinder **201** is introduced through the line **L101** into the film-forming chamber **101**, while ozone-containing oxygen gas is introduced from the ozone generator **202** through the line **L102** into the film-forming chamber **101**. A switching valve **V1** is disposed at the confluence of the line **L101** and the line **L102**. An oxygen cylinder **203** is connected through the line **L103** to the ozone generator **202**.

The system **30** for removing volatile ruthenium oxide is provided with a decomposition unit proper **301** whose interior defines at least one flow path **301a** for the exhaust gas stream that is discharged from the film-forming apparatus and that contains the volatile ruthenium oxide (gas) produced by cleaning. This decomposition unit proper **301** has a gas inlet **301b** and a gas outlet **301c**. The gas inlet **301b** is connected through the line **L301** to the gas exhaust port of the film-forming chamber **101**. A

heating unit (heater) **302** is disposed on the circumference of the decomposition unit proper **301** in order to heat the exhaust gas stream flowing from the film-forming apparatus into the gas flow path **301a**.

5 A pump **40** that transports the gas stream through the interior of the decomposition unit proper **301** is connected through the line **L302** downstream from the decomposition unit proper **301**. A pump as generally used in film-forming apparatuses can be directly used for this pump **40**. In other words, the decomposition unit proper can be placed between the film-forming chamber and pump in the usual pump-equipped gas exhaust system of a film-forming apparatus. An exhaust gas treatment facility **50** is
10 disposed downstream from the pump **40** through the line **L303**; this exhaust gas treatment facility **50** treats the exhaust gas stream outflowing from the decomposition unit proper **301**.

The decomposition unit proper **301** can be constituted of, for example, a tube **311**, as schematically illustrated in cross section in Figure 2. This tube **311** typically has
15 a cylindrical shape for the corresponding ease of use, but the tube **311** is not limited to this shape. The decomposition unit proper **301** may also be constituted of a honeycomb structure, again as described above. The tube **311** is composed of a heat-resistant material that is not corroded by the volatile ruthenium oxide (for example, quartz or stainless steel).

20 The exhaust gas treatment facility **50** removes gaseous species — other than the volatile ruthenium oxide — that can be present in the gas stream outflowing from the decomposition unit proper **301** after completion of the decomposition treatment thereon. The exhaust gas treatment facility **50** can be a wet- or dry-process exhaust gas facility

as known per se or a plasma facility as known per se. For example, active alumina is effective for the decomposition of ozone.

The interior of the film-forming apparatus **10** is thoroughly exhausted by the operation of the pump **40** once it becomes necessary to clean the film-forming apparatus **10** after execution of ruthenium film formation or ruthenium dioxide film formation, i.e., when it becomes necessary to remove a ruthenium-type deposit — at least the surface region of which comprises solid ruthenium oxide — residing on a constituent member of the film-forming apparatus. This is followed by the introduction into the film-forming chamber **101** of hydrogen gas from the hydrogen cylinder **201**, preferably along with inert gas as described above, and reduction of the solid ruthenium oxide in the ruthenium-type deposit to ruthenium metal.

The hydrogen gas is stopped post-reduction using the switching valve **V1** and the interior of the film-forming chamber **101** is thoroughly exhausted and purged with an inert gas such as nitrogen in order to remove hydrogen and hydrogen radical from the film-forming apparatus **10**.

Ozone-containing oxygen gas is then introduced from the ozone generator **202** into the film-forming chamber **101** by switching at the switching valve **V1**. The ruthenium metal is brought into contact with the ozone-containing oxygen gas and is oxidized and converted into volatile ruthenium oxide, which is discharged from the film-forming chamber **101**.

The decomposition unit proper **301** is heated to a prescribed temperature by the heater **302** and the volatile ruthenium oxide-containing exhaust gas stream from the film-forming chamber is introduced at a prescribed pressure into the decomposition unit

proper **301**. The volatile ruthenium oxide in the heated exhaust gas stream from the film-forming chamber is decomposed and converted into solid ruthenium oxide, which deposits on the inner walls of the decomposition unit proper **301**. The ozone that can be present in the exhaust gas stream from the film-forming chamber undergoes
5 decomposition when the heating temperature under consideration is at least 100°C.

A concentration detection unit **204**, whose purpose is to detect the concentration of volatile ruthenium oxide in the exhaust gas stream from the film-forming chamber **101**, is preferably also disposed between the film-forming chamber **101** and the decomposition unit proper **301**. This concentration detection unit **204** can comprise an
10 ultraviolet spectrometer, Fourier-transform infrared spectrometer, Raman spectrometer, or other known detection unit capable of measuring the concentration of the volatile ruthenium oxide. This concentration detection unit **204** enables the oxidizing gas to be stopped at the point at which volatile ruthenium oxide is no longer detected in the exhaust gas stream from the film-forming chamber **101**, which enables the
15 decomposition process to be carried out in an efficient manner.

A concentration detection unit **303** for detection of the volatile ruthenium oxide concentration is provided between the decomposition unit proper **301** and the pump **40**. As already noted above, this can be utilized to set the initial conditions for decomposition of the volatile ruthenium oxide and to support control of the
20 decomposition efficiency.

Figure 3 contains a schematic cross-sectional drawing that illustrates an example of a decomposition unit proper **301** that contains decomposition catalyst. A decomposition catalyst **312** comprising ruthenium metal or solid ruthenium oxide is

attached to the inner wall of the tube **311** constituting the decomposition unit proper **301**.

The procedure using a decomposition unit proper **301** provided with a decomposition catalyst **312** is substantially the same as the procedure already
5 described above. The volatile ruthenium oxide in the gas stream brought into contact with the decomposition catalyst **312** undergoes decomposition and is converted into solid ruthenium oxide, which deposits on the decomposition catalyst **312**.

Since volatile ruthenium oxide is toxic, the interior of the decomposition unit proper **301** is preferably maintained under reduced pressure based on safety
10 considerations. The pressure within the decomposition unit proper **301** need not be specifically controlled and can be the same as the pressure in the film-forming chamber **101**.

Figure 4 contains a block drawing that illustrates another example of a film-forming apparatus that is provided with a system that successively implements cleaning
15 of the film-forming apparatus and removal of the volatile ruthenium oxide in accordance with the present invention. Those elements in Figure 4 that are the same as in Figure 1 have been assigned the same reference symbols as in Figure 1 and will not be described in detail again.

The apparatus shown in Figure 4 has approximately the same structure as the
20 apparatus shown in Figure 1, with the exception that the decomposition unit proper **301** is disposed in a line **L401** that branches from the line **L301** rather than being connected in the line **L301** that connects to the film-forming chamber **101** and pump **40** as shown in Figure 1. The gas stream from the decomposition unit proper **301** connected in the

branch line **L401** flows into the line **L301** through the line **L402**, i.e., the line **L402** joins with the line **L301** upstream from the pump **40**. The line **L301** has a shut-off valve **V21** upstream from the point of confluence with the line **L402**, while a shut-off valve **V22** is provided in the line **L401** and a shut-off valve **V23** is provided in the line **L402**. A
5 concentration detection unit **204** is provided in the apparatus illustrated in Figure 4 on the line **L301** upstream from the branch point with the line **L401**.

The interior of the film-forming apparatus **10** is thoroughly exhausted by the operation of the pump **40** once it becomes necessary to clean the film-forming apparatus **10** after execution of ruthenium film formation or ruthenium dioxide film
10 formation, i.e., when it becomes necessary to remove a ruthenium-type deposit — at least the surface region of which comprises solid ruthenium oxide — residing on a constituent member of the film-forming apparatus. The shut-off valves **V22** and **V23** are closed during this phase. The shut-off valves **V22** and **V23** are of course also closed during the film formation phase.

15 Once the interior of the film-forming apparatus **10** has been thoroughly exhausted, reducing gas is introduced into the film-forming chamber **101** as described in relation to Figure 1 and the desired reduction is carried out. As described in relation to Figure 1, the hydrogen gas is stopped post-reduction using the switching valve **V1** and the interior of the film-forming chamber **101** is thoroughly exhausted and purged
20 with an inert gas such as nitrogen in order to remove hydrogen and hydrogen radical from the film-forming apparatus **10**. The shut-off valve **V21** is then closed and the shut-off valves **V22** and **V23** are opened and ozone-containing oxygen gas is introduced into the film-forming chamber **101** again as described in relation to Figure 1. The ruthenium

metal is brought into contact with the ozone-containing oxygen gas and is oxidized and converted into volatile ruthenium oxide, which is discharged from the film-forming chamber **101**. Decomposition of the volatile ruthenium oxide in the exhaust gas stream from the film-forming chamber is also carried out as already described above. Cleaning
5 is complete when volatile ruthenium oxide is no longer detected by the concentration detection unit **204**. Once cleaning has been completed, the flow of oxygen gas is stopped and the shut-off valves **V22** and **V23** are closed and preparation is made for the ensuing film fabrication process.

The concentration detection unit **204** is disposed in Figure 4 in the line **L301**
10 upstream from the branch point with the line **L401**, but this concentration detection unit **204** can be placed between the switching valve **V22** and the decomposition unit proper **301** when the exhaust gas stream from the film-forming chamber contains gas that would interfere with detection of the volatile ruthenium oxide concentration by the concentration detection unit **204**.

15 According to the inventive method for removing volatile ruthenium oxide, the volatile ruthenium oxide in a gas stream is decomposed into solid ruthenium oxide, which deposits within the decomposition unit. As a consequence, the solid ruthenium oxide can be easily recovered by removing the decomposition unit after the decomposition process, both in the case of a decomposition unit not provided with
20 decomposition catalyst and in the case of a decomposition unit containing a ruthenium metal or solid ruthenium oxide decomposition catalyst. This recovery has heretofore been problematic.

Examples

Examples of this invention are described below, but this invention is not limited by these examples.

5 Example 1

Chromium was deposited in a thickness of 500 Å as a bonding layer on the surface of a silicon substrate and ruthenium metal was then vapor-deposited thereon under reduced pressure to a thickness of 1000 Å. The formation of ruthenium dioxide in a thickness of 10-50 Å on the surface of the ruthenium metal was measured by Auger electron spectroscopy (AES).
10

This silicon substrate was installed in a cylindrical quartz tube (length = 60 cm, inner diameter = 1.5 cm) and hydrogen and nitrogen (carrier gas) were then passed through the quartz tube at 200°C/700 torr for 5 minutes. The hydrogen flow rate was 4 sccm and the nitrogen flow rate was 100 sccm. It was confirmed by AES that the result
15 of this treatment was the reduction of all the ruthenium dioxide in the surface region to ruthenium metal.

After the interior of the quartz tube had then been purged with nitrogen, ozone-containing oxygen gas (ozone content = 4.7 volume%) from a commercial ozone generator was passed at a flow rate of 150 sccm through the quartz tube at room
20 temperature/700 torr. During this process, the absorbance (wavelength = 376 nm) by ruthenium tetroxide in the effluent gas from the quartz tube was measured with a UV spectrophotometer. The results are reported in Figure 5. According to the results in Figure 5, almost no ruthenium oxide was observed at 120 seconds after the introduction

of the ozone-containing gas and the ruthenium oxide had completely disappeared after 150 seconds.

Example 2

5 Hydrogen and nitrogen (carrier gas) were passed for 10 minutes at 200°C/700 torr through a cylindrical quartz tube (length = 60 cm, inner diameter = 1.5 cm) whose inner wall carried ruthenium dioxide in a thickness of at least 10000 Å. The hydrogen flow rate was 4 sccm and the nitrogen flow rate was 100 sccm. It was confirmed by AES that the result of this treatment was the reduction of all the ruthenium dioxide to
10 ruthenium metal.

After the interior of the quartz tube had then been purged with nitrogen, ozone-containing oxygen gas (ozone content = 4.7 volume%) from a commercial ozone generator was passed at a flow rate of 150 sccm through the quartz tube at room
15 temperature/700 torr. During this process, the absorbance (wavelength = 376 nm) by ruthenium tetroxide in the effluent gas from the quartz tube was measured with a UV spectrometer. The results are reported in Figure 6. According to the results in Figure 6, ruthenium oxide was completely absent at 300 seconds (5 minutes) after the introduction of the ozone-containing oxygen gas.

20

Reference Example 1

(A) A decomposition unit (not provided with decomposition catalyst) comprising a cylindrical quartz tube with a length of 60 cm and an inner diameter of 1.5 cm was

used in this procedure. Nitrogen carrier gas containing a constant proportion of ruthenium tetroxide was introduced into the cylindrical tube at a flow rate of 10 sccm at different temperatures and pressures (5-20 torr) in the cylindrical tube. The ruthenium tetroxide concentration in the gas stream flowing out of the decomposition unit was measured with an ultraviolet spectrometer. Curve **a** in Figure 7 reports the relationship between the ruthenium tetroxide concentration in the outflowing gas stream and the heating temperature wherein the ruthenium tetroxide concentration in the initial gas stream is designated as 100. About the same results as reported by curve **a** were obtained regardless of the pressure in the decomposition unit (5-20 torr).

As shown by the curve **a** results in Figure 7, ruthenium tetroxide was almost completely removed in this reference example at temperatures \geq about 215°C.

- (B) A pressure of 700 torr was then established in the same decomposition unit and oxygen containing 4.7 volume% ozone was introduced at a flow rate of 150 sccm into the decomposition unit at different temperatures in the decomposition unit. The ozone concentration in the gas stream flowing out of the decomposition unit was measured with an ultraviolet spectrometer. The results showed that the ozone was about 99% decomposed at a heating temperature of 100°C and was 100% decomposed at a heating temperature of 140°C. This confirmed that ozone and ruthenium tetroxide could be simultaneously removed by the thermal decomposition unit.

Reference Example 2

The same procedure as in Reference Example 1(A) was carried out with the exception that a decomposition unit as described in Example 2 was used (cylindrical
5 quartz tube whose inner wall carried ruthenium dioxide in a thickness of at least 10000 Å). The results are reported by curve **b** in Figure 7. About the same results as reported by curve **b** were obtained regardless of the pressure in the decomposition unit (5-20 torr).

As shown by the curve **b** results in Figure 7, ruthenium tetroxide was almost
10 completely removed by decomposition in this reference example at temperatures \geq about 150°C.

Brief Description of the Drawings

Figure 1 contains a block drawing that illustrates an example of the structure of a
15 film-forming apparatus that is provided with a system for carrying out the cleaning method according to the present invention.

Figure 2 contains a schematic cross-sectional drawing that illustrates an example of a decomposition unit that can be used for the removal according to the present invention of volatile ruthenium oxide.

20 Figure 3 contains a drawing that illustrates, in a partial cross-sectional side view, another example of a decomposition unit that can be used for the removal according to the present invention of volatile ruthenium oxide.

Figure 4 contains a block drawing that illustrates another example of the structure of a film-forming apparatus that is provided with a system for carrying out the cleaning method according to the present invention.

5 Figure 5 contains a graph that shows the relationship obtained in Example 1 between the treatment time and the absorbance indicative of the concentration of volatile ruthenium oxide in the gas outflowing from a film-forming chamber.

Figure 6 contains a graph that shows the relationship obtained in Example 2 between the treatment time and the absorbance indicative of the concentration of volatile ruthenium oxide in the gas outflowing from a film-forming chamber.

10 Figure 7 contains a graph that shows the relationship between temperature and the concentration of volatile ruthenium oxide in the gas outflowing from a decomposition unit.